

November 26, 2012

Pamela Creedon, Executive Officer
Joe Karkoski, Assistant Executive Officer
Central Valley Regional Water Quality Control Board
11020 Sun Center Drive, #200
Rancho Cordova, CA 95670-6114

Dear Ms. Creedon,

The East San Joaquin Water Quality Coalition (ESJWQC or Coalition) requests three changes to its monitoring program that will require an amendment to the Monitoring and Reporting Program Plan (MRPP) and associated Quality Assurance Project Plan (QAPP). The Coalition requests to update sample preservation temperatures to be consistent with EPA method requirements, to update preservation and holding requirements for sediment chemistry and sediment Total Organic Carbon (TOC) analysis, and to update the analytical method for triazines to EPA 8141A.

Preservation Temperature Requirements

The Irrigated Lands Regulatory Program (ILRP) Monitoring and Reporting Program (MRP) Order No. R5-2008-0005 specifies preservation temperature requirements as “4°C” for all surface water and sediment analyses. Based on the most recent method requirements, the Coalition is requesting to update the temperature requirements from 4°C to ≤6°C for all analytical parameters except for *E. coli*. The Coalition is requesting an update for the temperature requirement for *E. coli* analysis to be updates from 4°C to <8°C.

Bacteria (E. coli)

The Coalition is requesting to change the temperature holding requirement for *E. coli* to <8°C based on most recent published requirements for Collection and Preservation of Samples for Microbiological Examination in the *Standard Methods for the Examination of Water and Wastewater* (SM 9060) which specifies a holding temperature of “at < 8°C” for *E. coli* samples (the most recent updates to the *Standard Methods* is only available online by subscription; see Enclosure). The Coalition is not requesting a change to the current holding time requirement of 24 hours since it is not logistically possible to collect and deliver samples to the analytical laboratory within a shorter period. A study done on the *Assessment of the Effects of Holding Time and Temperature on Escherichia coli Densities in Surface Water Samples* (Pope et al. 2003), listed in the bibliography of SM 9060, found that samples held with a holding time greater than 8 hours can produce comparable data to samples held within an 8 hour hold time as long as they are kept below 10°C. The laboratory analyzes the bacteria samples as soon as they arrive, which equates to a holding time range of 16 hours to 24 hours.

General Analytical Parameters

For all other parameters the Coalition is requesting to update the temperature holding temperature requirement to $\leq 6^{\circ}\text{C}$ as per the most recent revised methods listed in the Federal Register. Federal Register Vol. 72, No. 47 Rules and Regulations issued on March 12, 2007 revised some methods and analysis procedures in 40 CFR Part 136, and included an update to the temperature preservation requirements from “Cool, 4°C ” to “Cool, $\leq 6^{\circ}\text{C}$ ” (Table II, page 11236-11239). The update rules are consistent with Standard Method preservation requirements “Refrigerate = storage at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$; in the dark” (Table 1060:I, Standard Methods 20th ed.). Footnote 18 of 40 CFR Part 136 (Table II, page 11239) reads:

"Aqueous samples must be preserved at $\leq 6^{\circ}\text{C}$, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of “ $\leq^{\circ}\text{C}$ ” is used in place of the “ 4°C ” and “ $<4^{\circ}\text{C}$ ” sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that rounding down to 6°C may not be used to meet the $\leq 6^{\circ}\text{C}$ requirement. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes)."

The Coalition requests to amend the temperature preservation requirements to be consistent with 40 CFR Part 136 and Standard Methods. Table 1 lists the current preservation requirement and requested changes. Once approved, the Coalition will submit an updated QAPP.

Initial Preservation/Holding Requirements for Sediment TOC and Sediment Chemistry

The ILRP MRP Order No. R5-2008-0005 specifies preservation and hold time requirements for sediment TOC chemistry and sediment chemistry analysis as “can be held at 4°C for up to 48 hours, and should be analyzed within this 48 hour period, but can be frozen at any time during the initial 48 hours for up to 12 months maximum at -20°C ” (MRP Appendix E, Attachment C). The Coalition requests to amend the preservation and hold time requirements for sediment total organic carbon (TOC) and sediment chemistry to be consistent with current method requirements.

Sediment TOC

The Coalition requests to amend the preservation and hold time requirements for sediment TOC chemistry analysis to “store at $\leq 6^{\circ}\text{C}$ (not frozen), analyze or freeze (-20°C) within 28 days” (Table 1) to be consistent with the hold time listed in the 2008 SWAMP QAPrP and the standard methods used for analysis (2008 SWAMP QAPrP, Table B4). The Walkley Black Method SOP for TOC specifies a maximum hold time of 28 days (page 4; See Enclosure).

Sediment Chemistry (pyrethroids and chlorpyrifos)

The Coalition requests to amend the preservation and hold time requirements for sediment chemistry analysis to “store at ≤6°C (not frozen), extract within 14 days or freeze (-20°C) within 48 hours” to be consistent with the hold time listed in the 2008 SWAMP QAPrP and the standard methods used for analysis. The 2008 SWAMP QAPrP recommends sediment sample preservation for organophosphate pesticides and pyrethroids analysis as “1 year at -20°C; Samples must be extracted within 14 days of collection and extracts analyzed within 40 days following extraction” (page 125-126, Table B25 and B30). The EPA’s *Test Methods for Evaluation Solid Waste, Physical/Chemical Methods* (SW-846) specifies that sediment samples for semivolatile organics analyses (USEPA 8270 and 8081) should be extracted within 14 days.

Table 1 below lists the current preservation requirement and requested changes. Once approved, the Coalition will submit an amended QAPP.

Table 1. Preservation and holding requirements; requested updates compared to current QAPP requirements.

Analytical Parameter	Initial Preservation/Holding Requirements- Current QAPP	Initial Preservation/Holding Requirements- Requested Update
Total Dissolved Solids	Store at 4°C	Store at ≤6°C
Total Suspended Solids		
Turbidity		
Soluble Orthophosphate		
TKN, Ammonia, Total Phosphorus, Nitrate-Nitrite as N	Preserve to ≤pH 2 with H ₂ SO ₄ , store at 4°C	Preserve to ≤pH 2 with H ₂ SO ₄ , store at ≤6°C
Metals/Trace Elements, Hardness	Filter as necessary; preserve to ≤pH 2 with HNO ₃ , store at 4°C	Filter as necessary; preserve to ≤pH 2 with HNO ₃ ; store at ≤6°C
<i>E. coli</i> (pathogens)	Store at 4°C	Store at < 8°C
Total Organic Carbon	Preserve with HCl, store at 4°C	Preserve with HCl, store at ≤6°C
Carbamates	Store at 4°C; extract within 7 days	Store at ≤6°C; extract within 7 days
Organochlorines		
Organophosphates		
Herbicides (general)		
Herbicides (paraquat dichloride)	Store at 4°C; extract within 7 days	Store at ≤6°C; extract within 7 days
Herbicides (glyphosate)	Store at 4°C; freeze (-20°C) within 2 weeks	Store at ≤6°C; freeze (-20°C) within 2 weeks
Aquatic Toxicity	Store at 4°C	Store at ≤6°C
Sediment Toxicity	Store at 4°C, do not freeze	Store at ≤6°C, do not freeze
Sediment Grain Size	Store at 4°C, do not freeze	Store at ≤6°C, do not freeze
Sediment Total Organic Carbon	Store at 4°C, freeze (-20°C) within 48 Hours	Store at ≤6°C or freeze (-20°C) within 28 days
Sediment Chemistry	Store at 4°C, freeze (-20°C) within 48 Hours	Store at ≤6°C (not frozen), extract within 14 days or freeze (-20°C) within 48 hours

Triazine Organics Method

Method EPA 8141 is listed in the ILRP MRP Order No. R5-2008-0005 as an optional method for analysis of simazine but not for atrazine or cyanazine. The ESJWQC is requesting to update their MRPP and associated QAPP to list EPA 8141A as an optional analysis method for atrazine, cyanazine and simazine.

Agriculture & Priority Pollutants Laboratories, Inc. (APPL) is contracted by the ESJWQC to analyze the list of pesticides included in the ILRP MRP. Triazines are currently analyzed with method EPA 619; however, the California Environmental Laboratory Accreditation Program (CA-ELAP) is no longer certifying this method.

APPL will renew its CA-ELAP certifications in January 2013 and at that time will begin analyzing triazines with EPA 8141A.

Methods EPA 619 and 8141A are very similar and use the same analysis instrument, columns and running conditions. The main differences between the two methods are the quality control criteria. EPA 619 has more stringent second source criteria (10% rather than the 20% allowed by EPA 8141A) and continuing calibration verification criteria (15% rather than the 20% allowed by EPA 8141A). However, EPA 619 has less stringent initial calibration requirements (3 point calibration rather than the 5 point required by EPA 8141A).

APPL has sufficient documentation that method EPA 8141A will meet performance requirements for atrazine, cyanazine and simazine. When APPL renews its CA-ELAP certification in January 2013, atrazine will be added to the list of compounds under their EPA 8141 certification. Simazine is already included under APPL's EPA 8141 certification. CA-ELAP is no longer offering a certification for cyanazine by any method. APPL will institute a Quality-Assurance Quality Control (QA/QC) Program for cyanazine analyzed by EPA 8141A and will maintain a manual containing the steps followed in APPL's QA/QC Program in the laboratory that will be available for inspection by Central Valley Regional Water Quality Control Board staff, per the instructions in the MRP Order Attachment C for analyses performed by a noncertified laboratory (II. Objective section, page 4). The data quality objectives for triazines analyzed by EPA 8141A are included in Table 2 and remain the same as those approved for EPA 619. A Quality Control package for triazines analyzed by EPA 8141A is submitted as an attachment to this letter.

Once approved, the Coalition will submit an updated QAPP and EPA 8141A Standard Operating Procedure (SOP).

Table 2. Data quality objectives for atrazine, cyanazine and simazine analyzed by either EPA 619 or EPA 8141 (Table 5 in the current ESJWQC QAPP).

Constituent	Matrix	Matrix Spike Frequency [†]	Lab Control Spike Frequency	Accuracy/ Recovery	Lab Duplicate Frequency	Precision	Completeness
Atrazine	Fresh Water	1 per batch	1 per batch	39-156%	1 per batch	RPD ≤ 25%	90%
Cyanazine	Fresh Water	1 per batch	1 per batch	22-172%	1 per batch	RPD ≤ 25%	90%
Simazine	Fresh Water	1 per batch	1 per batch	21-179%	1 per batch	RPD ≤ 25%	90%



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Additional Information and References

March 12, 2007 Federal Register notice:

<http://www.epa.gov/fedrgstr/EPA-WATER/2007/March/Day-12/w1073.htm>

Online access to the most recent Standard Methods (subscription required):

<http://www.standardmethods.org/store/>

Pope, M.L., M. Bussen, M.A. Feige, L. Shadix, S. Gonder, C. Rodgers, Y. Chambers, J. Pulz, K. Miller, K. Connell & J. Standridge. 2003. Assessment of the effects of holding time and temperature on *Escherichia coli* in surface water samples. *Appl. Environ. Microbiol.* 69:6201. (Available for download at <http://aem.asm.org/>)

Please let us know if you require further information.

Submitted respectfully,

Parry Klassen
Executive Director
East San Joaquin Water Quality Coalition

CC: Jelena Hartman, CVRWQCB

Enclosures:

2008 Surface Water Ambient Monitoring Program (SWAMP) QAPrP
2009 Determination of TOC by Walkley-Black Method Internal Operating Procedure
2012 SW-846 8270 Method
EPA 8141A Quality Control Package for Triazines
Standard Methods for the Examination of Water and Wastewater- Online Edition (SM 9060 excerpt)